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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08G 77/12, 77/04</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/47945</b> <b>(43) International Publication Date:</b> 29 October 1998 (29.10.98)
<b>(21) International Application Number:</b> PCT/US98/06490 <b>(22) International Filing Date:</b> 2 April 1998 (02.04.98)  <b>(30) Priority Data:</b> 60/044,482 21 April 1997 (21.04.97) US 09/044,831 20 March 1998 (20.03.98) US  <b>(71) Applicant:</b> ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). <b>(72) Inventors:</b> HACKER, Nigel, P.; 13030 Footll Avenue, San Martin, CA 95046 (US). LEFFERTS, Scott; 188 North Sunnyvale Avenue, Sunnyvale, CA 94086 (US). FIGGE, Lisa; 706 Oak Grove Avenue, Menlo Park, CA 94025 (US). <b>(74) Agent:</b> CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (E. Iannarone), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, GH, HU, ID, IL, IS, JP, KP, KR, LK, LR, LS, LT, LV, MG, MK, MN, MW, MX, NZ, PL, RO, RU, SD, SG, SI, SK, SL, TR, TT, UA, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ORGANOHYDRIDOSILOXANE RESINS WITH LOW ORGANIC CONTENT  <b>(57) Abstract</b>  An organohydridosiloxane polymer having a cage conformation, between approximately 0.1 to 40 mole percent carbon-containing substituent, and a dielectric constant of less than about 3.0 is disclosed. Each silicon atom of the cage polymer is bonded to at least three oxygen atoms and to either a hydrogen atom or an organic substituent. By providing such a caged structure having essentially no hydroxyl or alkoxy substituents, either on the polymer backbone or at terminal silicon atoms, essentially no chain lengthening polymerization can occur in solution. Such organohydridosiloxane resins having a molecular weight in the range from about 400 to about 200,000 atomic mass units were formed using a dual phase solvent system and either a solid phase or a phase transfer catalyst to assist the condensation of hydridotrihalosilane with at least one organotrihalosilane.		

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## ORGANOHYDRIDOSILOXANE RESINS WITH LOW ORGANIC CONTENT

### BACKGROUND OF THE INVENTION

#### 5 Cross Reference to Related Applications

This application is the non-provisional application of related provisional application entitled "HYDROGENSILOXANE RESINS WITH LOW ORGANIC CONTENT," provisional serial number 60/044482, filed on April 21,  
10 1997 the benefit of whose priority date is hereby claimed, and the disclosure of which is incorporated by reference herewith.

A related application entitled "ORGANOHYDRIDOSILOXANE RESINS WITH HIGH ORGANIC  
15 CONTENT", by the inventors of the present application, Attorney Docket No. 30-4305(4780), is filed concurrently herewith.

### Field of the Invention

20 The present invention relates generally to siloxane based resins, and more specifically to a caged conformation organohydridosiloxane composition, methods for the synthesis thereof, and low dielectric constant films formed therefrom.

#### 25 Description of the Related Art

Semiconductor devices often have one or more arrays of patterned interconnect levels that serve to electrically couple the individual circuit elements thus forming an integrated circuit (IC). These

interconnect levels are typically separated by an insulating or dielectric film. Previously, a silicon oxide film formed using chemical vapor deposition (CVD) or plasma enhanced CVD (PECVD) techniques was the most commonly used material for such dielectric films. However, as the size of circuit elements and the spaces between such elements decreases, the relatively high dielectric constant of such silicon oxide films is problematic.

10 In order to provide a lower dielectric constant than that of silicon oxide, dielectric films formed from siloxane based resins are becoming widely used. One such family of films formed from siloxane based resins are the films derived from hydrogen siloxane (HSQ) resins (See, U.S. Pat. No. 3,615,272, Oct. 19, 15 1971, Collins et al.; and U.S. Pat. No. 4,756,977, Jul. 12, 1988, Haluska et al.) However, while such films do provide lower dielectric constants than CVD or PECVD silicon oxide films and also provide other benefits 20 such as gap filling and surface planarization, it has been found that typically the dielectric constants of such films are limited to approximately 3.0 or greater (See, U.S. Pat. No. 5,523,163, Jun. 4, 1996, Ballance et al.).

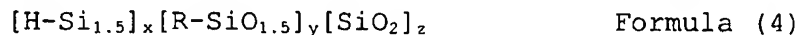
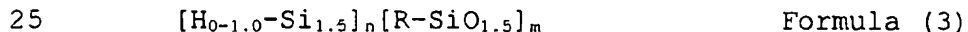
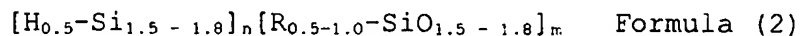
25 As known, the dielectric constant of such insulating films is an important factor where IC's with low power consumption, cross-talk, and signal delay are required. As IC dimensions continue to shrink, this factor increases in importance. As a result, siloxane based resin materials, and methods for making such 30 materials, that can provide insulating films with dielectric constants below 3.0 are very desirable. In addition, it would be desirable to have a siloxane based resin, and method for making the resin, that

provides such low dielectric constant films which additionally have a high resistance to cracking. It would also be desirable for such films to have low stress when formed in thicknesses of approximately 1.0 micron ( $\mu\text{m}$ ) or greater. It would also be desirable for such a siloxane based resin, and method for making, to provide low dielectric constant films via standard processing techniques. In this manner curing processes that require an ammonia or ammonia derivative type of atmosphere, or other non-standard type of semiconductor process, are avoided.

#### SUMMARY

In accordance with the present invention, organohydridosiloxane resins, and methods for making such resin, are provided. Solutions of such organohydridosiloxane resins are employed for forming caged siloxane polymer films useful in the fabrication of a variety of micro-electronic devices, particularly semiconductor integrated circuits.

The organohydridosiloxane resins of the present invention have the general formulas:



wherein:

- the sum of n and m, or the sum of x, y and z is from about 8 to about 5000, and m or y is selected such that carbon containing constituents are present in an amount of less than about 40 percent; R is selected

from substituted and unsubstituted, normal and branched alkyls, cycloalkyls, aryls, and mixtures thereof; and wherein the specific mole percent of carbon containing substituents is a function of the ratio of the amounts of starting materials. In some embodiments, particularly favorable results are obtained with the mole percent of carbon containing substituents being in the range of between about 15 mole percent to about 25 mole percent.

10        Polymers in accordance with the present invention have a polymer backbone encompassing alternate silicon and oxygen atoms. In contrast with previously known organosiloxane resins, polymers of the present invention have essentially no hydroxyl or alkoxy groups  
15        bonded to backbone silicon atoms. Rather, each silicon atom, in addition to the aforementioned backbone oxygen atoms, is bonded only to hydrogen atoms and/or R groups as defined in Formulae 1, 2, 3 and 4. By attaching only hydrogen and/or R groups directly to backbone  
20        silicon atoms in the polymer, unwanted chain lengthening and cross-linking is avoided. Consequently, the shelf life of organohydridosiloxane resin solutions in accordance with the present invention is enhanced as compared to previously known  
25        organosiloxane resins. Furthermore, since silicon-carbon bonds are less reactive than silicon hydrogen bonds, the shelf life of the organohydridosiloxane resin solutions in accordance with the present invention is enhanced as compared to previously known  
30        hydridosiloxane resins.

In some embodiments, the polymer backbone conformation is a cage configuration. Accordingly, there are only very low levels or reactive terminal moieties in the polymer resin of this invention. This

also ensures that no unwanted chain lengthening polymerization will occur in solution, resulting in an extended shelf life. Each silicon atom of the polymer is bonded to at least three oxygen atoms. Moieties  
5 bonded to the polymer backbone include hydrogen and organic moieties.

The organic moiety of the organotrichlorosilane monomer is alkyl or aryl and includes, but is not limited to, methyl, ethyl; linear and branched propyl,  
10 butyl, pentyl hexyl; and cyclic compounds such as cyclohexyl and phenyl. In some embodiments of the present invention, more than two of the aforementioned starting materials are employed.

In accordance with the method of this invention,  
15 synthesis of the organohydridosiloxane composition of this invention includes a dual phase solvent system using a catalyst. In some embodiments of the present invention, the starting materials encompass trichlorosilane and an organotrichlorosilane, for  
20 example either an alkyl or an aryl substituted trichlorosilane. The relative ratios of the trichlorosilane and the organotrichlorosilane determine the mole percent carbon-containing substituents in the polymer.

25 In some embodiments, the method of this invention includes:

- 1) mixing a solution of hydridotrihalosilanes and organic-substituted trihalosilanes (e.g. trichlorosilane and alkyl or aryltrichlorosilane) to  
30 provide a mixture,

- 2) combining the mixture with a dual phase solvent including a non-polar solvent, and a polar solvent to provide a dual phase reaction mixture,

3) adding a solid phase catalyst to the silane/solvent reaction mixture,

4) reacting the silanes to produce organohydridosiloxanes, and

5) recovering the organohydridosiloxane from the organic portion of the dual phase solvent system.

Additional steps may include washing the recovered organohydridosiloxane to remove any unreacted monomer, and fractionating the organohydridosiloxane product to thereby classify the product according to molecular weight.

In other embodiments, the catalyst is a phase transfer catalyst including, but not limited to, tetrabutylammonium chloride, and benzyltrimethylammonium chloride. The phase transfer catalyst is introduced into the reaction mixture and the reaction is allowed to proceed to the desired degree of polymerization.

In accordance with one aspect of the method of this invention, a dual phase solvent system includes a continuous phase non-polar solvent and a polar solvent. The non-polar solvent includes, but is not limited to, any suitable alkyl or aryl compounds or a mixture of any or all such suitable compounds, the operational definition of "suitable" in the present context includes the functional characteristics of:

- 1) solubilizing the monomeric silicon compounds,
- 2) solubilizing the resin product,
- 3) stability of the resin product in the solvent,

and

- 4) insolubility of unwanted reaction products.
- Exemplary solvents include, but are not limited



to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride, and mixtures thereof.

The second solvent phase is a polar phase,  
5 immiscible with the organic, non-polar solvent phase, and includes water, alcohols, and alcohol and water mixtures. It is thought that alcohol solubilizes reactive intermediates that are not yet soluble in the non-polar phase and would ordinarily be unstable in a  
10 substantially aqueous phase. The amount of alcohol present is, however, not so high as to significantly dissolve product polymers having molecular weights greater than about 400 AMUs.

Alcohols and other polar solvents suitable for use  
15 in the polar phase include, but are not limited to, water, methanol, ethanol, isopropanol, glycerol, diethyl ether, tetrahydrofuran, diglyme and mixtures thereof. In one embodiment, the polar solvent includes a water/alcohol mixture wherein the water is present in  
20 an amount sufficient to preferentially solubilize ionic impurities not soluble in alcohol, and/or preclude solvent extraction of product compounds that might otherwise be soluble in alcohol. The polar solvent phase advantageously retains the hydrochloric acid  
25 (HCl) condensation product and any metal salt or other ionic contaminants, that may be present. Since any ionic contaminants are retained in the polar solvent phase, the organohydridosiloxane product of this invention is of high purity and contains essentially no  
30 metal contaminants.

In accordance with another aspect of the method of the present invention, in one embodiment, a solid phase catalyst, such as Amberjet 4200, or Amberlite I-6766

ion exchange resin (both available from Rohm and Hass Company, Philadelphia, Pennsylvania), surface catalyzes the polymerization of the trihalosilane and organo-trihalosilane monomers into the composition of this invention. Amberjet 4200 is a basic anion exchange resin based on the chloride ion. Amberlite I-6766 is a also a basic anion exchange resin. By way of explanation, and not by way of limitation, it is thought polymer chain propagation occurs on the catalyst surface by hydrolysis of the Si-Cl bond of the monomer to Si-OH, followed by condensation with another Si-OH to provide an Si-O-Si bond, thereby extending the polymer chain. In other embodiments, polymerization is catalyzed with a phase transfer catalyst such as tetrabutylammonium chloride.

In embodiments of the present invention, the amount of organotrichlorosilane monomer present is an amount sufficient to provide an as-cured dielectric film having an organic content of less than about 40 mole percent carbon containing substituents. Such dielectric films formed in accordance with the present invention advantageously provide low dielectric constants, typically less than 3.0. In some embodiments, particularly alkylhydrosiloxane embodiments, the carbon-containing substituent content is a function of the mole percent alkyl- or aryltrihalosilane.

Additionally, dielectric films in accordance with the organohydrosiloxane composition of this invention exhibit thermal stability permitting cure temperatures up to about 450 ° centigrade.

This invention describes a new class of organohydrosiloxane resins having less than about 40

mole percent carbon-containing substituents. These new resins have improved stability giving longer shelf-life in solution. They also have much lower dielectric constants that are more stable after high temperature treatment than resins with no organic content.

#### DETAILED DESCRIPTION

While the invention is described hereinbelow with reference to certain embodiments, it is understood that these embodiments are presented by way of example and not by way of limitation. The intent of the following detailed description is to cover all modifications, alternatives and equivalents as may fall within the spirit and scope of the invention. For example, it is understood that although the examples use a chlorinated silane monomer, other monomers such as trifluorosilane, tribromosilane, organo-trifluorosilane, and organo-tribromosilane may be used. It is also understood that although an ethanol/water solution is typically used as the polar solvent, other alcohols and alcohol/water solutions may also be used.

#### **Experimental Methods**

The following characteristics encompass non-limiting measurements that illustrate the properties of the organohydridosiloxane polymer resins and thin films of the present invention. The methods used in measuring the various characteristics of the organohydridosiloxane resin and polymer films are as follows:

1) Film Thickness (A): Film thickness is measured using a calibrated Nanospec® AFT-Y CTS-102

model 010-180 Film Thickness Measurement System available from Nanometrics, Co. An average of measurements at five locations on a wafer are reported as the film thickness for each sample.

5           2) Molecular Weight ("MW"): Molecular weight is determined using a gel phase chromatography system from Waters Corporation, Milford, MA, equipped with a Waters 510 pump, Waters 410 differential refractometer and a Waters 717 autosampler. The procedure used is as set  
10 forth by S. Rosen in "Fundamental Principles of Polymeric Materials, pages 53-81, (2nd Ed. 1993) and incorporated herein by reference.

          3) Dielectric Constant: Dielectric constant is determined using the capacitance-voltage ("CV")  
15 measurement technique and employs a Hewlett-Packard Model 4061A semiconductor measurement system at a frequency of 1 MHz. This test procedure employs a metal-insulator-metal (MIM) structure with the thickness of each layer ranging from about 0.3 to  
20 1 micron ( $\mu\text{m}$ ).

#### Method Of Making and Examples

The method of making the compositions of the present invention include, generally, adding a mixture  
25 of the organotrihalosilane and hydridotrihalosilane (e.g. trichlorosilane and methyl trichlorosilane) to a mixture of catalyst, non-polar solvent, and polar solvent to form a reaction mixture. The polymerization reaction is allowed to proceed. Upon completion of the  
30 polymerization reaction, the reaction mixture is filtered, the polar solvent is separated, and the solution is dried and then evaporated to leave a white solid. This solid may then be slurried in hydrocarbon

solvent to remove monomer, and finally evaporated to leave the desired product.

The Mw of the product produced can be varied between 400 and 200,000 AMU depending on the reaction conditions. We have found that materials with molecular weights of 10,000 AMU, 20,000 AMU, 40,000 AMU and 60,000 AMU all have good coating properties.

In one embodiment, the organohydridosiloxane is formulated in a suitable solvent for use as a spin-on-dielectric polymer.

### Examples

The following examples describe the synthesis of the various organohydridosiloxane compositions of the present invention. Physical characteristics of the variously formed compositions were compared to hydridosiloxane control samples having no organic content. The control hydridosiloxane samples were prepared according to the following method:

#### Control

##### Hydridosiloxane Polymer for Dielectric Constant

##### Measurement

A 6L jacketed reactor equipped with a nitrogen inlet, dry ice condenser and a mechanical stirrer is charged with 5500 ml hexanes 440 ml ethanol, 142 ml water and 330 g Amberjet 4200 catalyst. This mixture is equilibrated for 0.5 hr with stirring at 25 °C. Trichlorosilane (380g, 2.80 mol) is added to the reactor using a peristaltic pump over a period of 55 minutes. Upon completion of the silane addition, hexane is pumped through the lines for 10 minutes. The reaction is stirred for 100 min, the ethanol/H<sub>2</sub>O layer

is removed then the hexane solution is filtered through a 3 micron filter followed by a 1 micron filter. The filtered solution is dried by flowing through a column of 4Å molecular sieves (400g) for 2.5h and then  
5 filtered through a 0.05um filter. The hexanes are removed using a rotary evaporator to give a white solid product (131g). Mw was measured by GPC as 21035 AMU with a polydispersity of 7.39. (Notebook # GD1.077 11/13/96.)

10        Example 1 and Example 2 describe the synthesis of methyl-hydridosiloxane, and in particular, clearly illustrates how the percent carbon incorporated into the product resin may be controlled by adjusting the initial mole percent of organic-substituted monomer.  
15 By adjusting the ratio of the relative amounts of starting monomers, the mole percent of carbon-containing substituents in the product resin is controlled. It is understood by one skilled in the art that the same means for controlling percent carbon  
20 (adjusting the mole ratio of the monomer starting materials) may be used for other organohydridosiloxane species such as cycloalkyl-substituted organohydridosiloxanes, and aryl-substituted organohydridosiloxanes.

25

### Varying Molar Amounts of Methyl Substituents

Example 1 through Example 12 describe the synynthesis of various methylhydridosiloxanes by varying the moles percent methyltrichlorosilane as a starting material. Examples 1-4, 6-12 used a solid phase catalyst in the reaction system, whereas Example 5 used a phase transfer catalyst.

Example 13 through Example 21 describe the formation of organohydridosiloxane resins using varying mole amounts of varying organic substituents.

#### Example 1

##### Preparation of 25 Mole Percent Methylhydridosiloxane

A 250mL Morton flask was fitted with a condenser and a stirrer connected to an Arrow 1750 motor. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 15g of Amberlite I-6766 ion exchange resin catalyst, 20mL of ethanol, 6.3mL of water, and 250mL of hexanes were added to the flask, and stirring was started. 13mL(0.129 mol.) of trichlorosilane and 5mL(0.043 mol.) of methyltrichlorosilane (24.9 mol% methyltrichlorosilane) were combined together in an HDPE bottle. This mixture of silanes was added to the Morton flask through a peristaltic pump at a rate of 0.6 mL/min. After addition was completed, stirring was continued for 90 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 40g of 3Å molecular sieves for 2.5 hr. Solution was filtered by vacuum through a Whatman #1

filter paper in a buchner funnel. Solution was evaporated on a Buchi rotary evaporator at 60C. 5.2g of white solid was collected. Mw was measured by GPC as 12,300 AMU with a polydispersity of 4.35.

5

### Example 2

#### **Preparation of 20 Mole Percent Methylhydridosiloxane**

A 2L Morton flask was fitted with a dry-ice condenser and a stirrer connected to an Arrow 1750 motor. Reactor was placed in a water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.25g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL of ethanol, 25mL of water, and 1000mL of hexanes were added to the flask, and stirring was started. 58mL(0.575 mol.) of trichlorosilane and 17mL(0.145 mol.) of methyltrichlorosilane (20.1 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the Morton flask by peristaltic pump through a 1/4" Teflon tube at a set rate of 8.0 RPM. Calculated addition rate was 2.5 mL/min. After addition was completed, stirring was continued for 185 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171g of 4Å molecular sieves for 3.5 hr. Solution was filtered by vacuum through a Whatman #2 filter paper in a buchner funnel. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 25.2g of white solid. Mw was measured by GPC as 26,014 AMU with a polydispersity of 13.68.



Example 3**Preparation of 20 Mole Percent Methylhydridosiloxane**

A 2L jacketed reactor was fitted with a dry-ice  
5 condenser, a stirrer connected to an Arrow 6000 motor,  
and a glass dip tube. Reactor was connected to a  
recirculating water bath set at 25C. The flask was  
purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown  
across the top of the condenser into an NaOH scrubber.  
10 103.9g of Amberjet 4200(Cl) ion exchange resin  
catalyst, 140mL of ethanol, 45mL of water, and 1750mL  
of hexanes were added to the reactor, and stirring was  
started. 100mL(0.991 mol.) of trichlorosilane and  
29mL(0.248 mol.) of methyltrichlorosilane (20 mol%  
15 methyltrichlorosilane) were combined together in an FEP  
bottle. This mixture of silanes was added to the  
reactor by peristaltic pump through a 1/4" Teflon tube  
at a set rate of 14.3 RPM. Calculated addition rate  
was 3.15 mL/min. After addition was completed,  
20 stirring was continued for 66 min. Solution was  
filtered by vacuum through a Whatman #4 filter in a  
buchner funnel. Solution was added to a separatory  
funnel and the lower, aqueous layer was discarded. The  
upper layer was dried over 299.7g of 4Å molecular  
25 sieves for 3 hr. Solution was filtered by vacuum  
through a Teflon membrane with 1 micron pores set on a  
glass frit. Solution was evaporated on a Buchi rotary  
evaporator at 60C. Yield was 53.2g of white solid. Mw  
was measured by GPC as 21,040 AMU with a polydispersity  
30 of 11.07.

Example 4

## Preparation of 20 Mole Percent Methylhydridosiloxane

A 2L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 850 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 52.65g of Amberjet 4200(Cl) ion exchange resin catalyst, 140mL of ethanol, 90mL of water, and 1750mL of hexanes were added to the reactor, and stirring was started. 200mL(1.982 mol.) of trichlorosilane and 58mL(0.496 mol.) of methyltrichlorosilane (20 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 10.0 RPM. Calculated addition rate was 2.4 mL/min. After addition was completed, stirring was continued for 48 min. Solution was filtered by vacuum through a Whatman #1 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 300g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 61.82g of white solid. Mw was measured by GPC as 16,999 AMU with a polydispersity of 17.21.

Example 5

## Preparation of 20 Mole Percent Methylhydridosiloxane

A 2L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 850 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 10.0g of 10% tetrabutylammonium chloride catalyst in water, 380mL of ethanol, 66mL of water, and 1500mL of hexanes were added to the reactor, and stirring was started. 171mL(1.694 mol.) of trichlorosilane and 50mL(0.426 mol.) of methyltrichlorosilane (20.1 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 11.5 RPM. Calculated addition rate was 2.95 mL/min. After addition was completed, stirring was continued for 130 min. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. Solution was filtered by vacuum through a Whatman #1 filter in a buchner funnel. The upper layer was dried over 303.2g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 77.5g of white solid. Mw was measured by GPC as 32,051 AMU with a polydispersity of 29.35.

Example 6Preparation of 16 Mole Percent Methylhydrosiloxane

A 2L Morton flask was fitted with a dry-ice condenser and a stirrer connected to an Arrow 1750  
5 motor. Reactor was placed in a water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.30g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL of ethanol, 25mL of water, and  
10 1000mL of hexanes were added to the flask, and stirring was started. 61mL of trichlorosilane (0.604 mol.) and 13.5mL (0.115 mol.) of methyltrichlorosilane (16 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the  
15 Morton flask by peristaltic pump through a 1/4" Teflon tube at a set rate of 8.5 RPM. Calculated addition rate was 2.33 mL/min. After addition was completed, stirring was continued for 180 min. Solution was filtered by vacuum through a Whatman #4 filter in a  
20 buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 170.63g of 4Å molecular sieves for 5.75 hr. Solution was filtered by vacuum through a Whatman #2 filter paper in a buchner funnel.  
25 Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 26.4g of white solid. Mw was measured by GPC as 26,813 AMU with a polydispersity of 14.20.

Example 7

## Preparation of 12 Mole Percent Methylhydridosiloxane

A 2L Morton flask was fitted with a dry-ice condenser and a stirrer connected to an Arrow 1750  
5 motor. Reactor was placed in a water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.32g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL of ethanol, 25mL of water, and  
10 1000mL of hexanes were added to the flask, and stirring was started. 63mL(0.624 mol.) of trichlorosilane and 10mL(0.085 mol.) of methyltrichlorosilane (12 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the  
15 Morton flask by peristaltic pump through a 1/4" Teflon tube at a set rate of 8.5 RPM. Calculated addition rate was 2.45 mL/min. After addition was completed, stirring was continued for 60 min. Solution was filtered by vacuum through a Whatman #4 filter in a  
20 buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171.63g of 4Å molecular sieves for 7 hr. Solution was filtered by vacuum through a Whatman #2 filter paper in a buchner funnel.  
25 Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 22.7g of white solid. Mw was measured by GPC as 24,089 AMU with a polydispersity of 15.84.

Example 8**Preparation of 10 Mole Percent Methylhydrosiloxane**

A 500mL Morton flask was fitted with a condenser and a stirrer connected to an Arrow 850 motor. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 18.03g of Amberjet 4200 (Cl) ion exchange resin catalyst, 20mL of ethanol, 6.3mL of water, and 250mL of hexanes were added to the flask, and stirring was started. 16mL(0.159 mol.) of trichlorosilane and 2mL(0.017 mol.) of methyltrichlorosilane (9.7 mol% methyltrichlorosilane) were combined together in an HDPE bottle. This mixture of silanes was added to the Morton flask through a peristaltic pump at a rate of 0.6 mL/min. After addition was completed, stirring was continued for 98 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 30.04g of 4Å molecular sieves for 3.25 hr. Solution was filtered by vacuum through a Whatman #1 filter paper in a buchner funnel. Solution was evaporated on a Buchi rotary evaporator at 60C. 5.9g of white solid was collected. Mw was measured by GPC as 15,844 AMU with a polydispersity of 4.57.

Example 9**Preparation of 8 Mole Percent Methylhydrosiloxane**

A 2L Morton flask was fitted with a dry-ice condenser and a stirrer connected to an Arrow 1750 motor. Reactor was placed in a water bath set at 25C.

The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.27g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL of ethanol, 25mL of water, and 5 1000mL of hexanes were added to the flask, and stirring was started. 66mL(0.654 mol.) of trichlorosilane and 7mL(0.060 mol.) of methyltrichlorosilane (8.35 mol% methyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the 10 Morton flask by peristaltic pump through a 1/4" Teflon tube at a set rate of 8.5 RPM. Calculated addition rate was 2.15 mL/min. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum through a Whatman #4 filter in a 15 buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 170.25g of 4Å molecular sieves for 3.25 hr. Solution was filtered by vacuum through a Whatman #2 filter paper in a buchner funnel. 20 Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 24.5g of white solid. Mw was measured by GPC as 23,066 AMU with a polydispersity of 15.50.

#### Example 10

##### 25 Preparation of 5 Mole Percent Methylhydrosiloxane

A 500mL Morton flask was fitted with a condenser and a stirrer connected to an Arrow 850 motor. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH 30 scrubber. 18.02g of Amberjet 4200 (Cl) ion exchange resin catalyst, 20mL of ethanol, 6.3mL Of water, and 250mL Of hexanes were added to the flask, and stirring was started. 17mL(0.168 mol.) of trichlorosilane and

1 mL (0.009 mol.) of methyltrichlorosilane (5.1 mol% methyltrichlorosilane) were combined together in an HDPE bottle. This mixture of silanes was added to the Morton flask through a peristaltic pump at a rate of  
5 0.6 mL/min. After addition was completed, stirring was continued for 90 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer  
10 was dried over 30.25g of 4Å molecular sieves for 2.5 hr. Solution was filtered by vacuum through a Whatman #4 filter paper in a buchner funnel. Solution was evaporated on a Buchi rotary evaporator at 60C. 6.6g of white solid was collected. Mw was measured by GPC  
15 as 18,947 AMU with a polydispersity of 4.60.

#### Example 11

##### **Preparation of 4 Mole Percent Methylhydridosiloxane**

A 2L Morton flask was fitted with a dry-ice  
20 condenser and a stirrer connected to an Arrow 1750 motor. Reactor was placed in a water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.40g of Amberjet 4200(Cl) ion exchange  
25 resin catalyst, 80mL of ethanol, 25mL of water, and 1000mL of hexanes were added to the flask, and stirring was started. 70mL (0.694 mol.) of trichlorosilane and 3.5mL (0.030 mol.) of methyltrichlorosilane (4.1 mol% methyltrichlorosilane) were combined together in an FEP  
30 bottle. This mixture of silanes was added to the Morton flask by peristaltic pump through a 1/4" Teflon tube at a set rate of 10.0 RPM. Calculated addition rate was 2.45 mL/min. After addition was completed,



stirring was continued for 60 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171.53g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Whatman #1 filter paper in a buchner funnel. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 25.1g of white solid. Mw was measured by GPC as 22,094 AMU with a polydispersity of 8.77.

### Example 12

#### **Preparation of 2 Mole Percent Methylhydrosiloxane**

A 2L jacketed reactor was fitted with a condenser and a stirrer connected to an Arrow 850 motor. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 105.07g of Amberjet 4200 (Cl) ion exchange resin catalyst, 140mL of ethanol, 45mL of water, and 1750mL of hexanes were added to the flask, and stirring was started. 123mL(1.219 mol.) of trichlorosilane and 3mL(0.026 mol.) of methyltrichlorosilane (2.1 mol% methyltrichlorosilane) were combined together. This mixture of silanes was added to the Morton flask through a peristaltic pump at a rate of 3.2 mL/min. After addition was completed, stirring was continued for 25 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 354.3g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Whatman #2 filter paper in a buchner funnel. Solution was evaporated on a Buchi

rotary evaporator at 60C. 42.00g of white solid was collected. Mw was measured by GPC as 21,312 AMU with a polydispersity of 4.80.

5 **Example 13**

**Preparation of 20 Mole Percent Ethylhydridosiloxane**

A 1L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 850 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was  
10 purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.6g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL of ethanol, 25mL of water, and 1000mL of hexanes  
15 were added to the reactor, and stirring was started. 58mL(0.575 mol.) of trichlorosilane and 19mL(0.145 mol.) of ethyltrichlorosilane (20.1 mol% ethyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the  
20 reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 11.2 RPM. Calculated addition rate was 2.2 mL/min. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel.  
25 Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit.  
30 Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 31.0g of white solid. Mw was measured by GPC as 23,987 AMU with a polydispersity of 10.27.

Example 14**Preparation of 20 Mole Percent Propylhydridosiloxane**

A 2L jacketed reactor was fitted with a dry-ice  
5 condenser, a stirrer connected to an Arrow 6000 motor,  
and a glass dip tube. Reactor was connected to a  
recirculating water bath set at 25C. The flask was  
purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown  
across the top of the condenser into an NaOH scrubber.  
10 59.5g of Amberjet 4200(Cl) ion exchange resin catalyst,  
80mL OF ethanol, 25mL of water, and 1000mL Of hexanes  
were added to the reactor, and stirring was started.  
58mL(0.575 mol.) of trichlorosilane and 21.5mL(0.145  
mol.) of propyltrichlorosilane (20.1 mol%  
15 propyltrichlorosilane) were combined together in an FEP  
bottle. This mixture of silanes was added to the  
reactor by peristaltic pump through a 1/4" Teflon tube  
at a set rate of 11.0 RPM. Calculated addition rate  
was 2.3 mL/min. After addition was completed, stirring  
20 was continued for 120 min. Solution was filtered by  
vacuum through a Whatman #4 filter in a buchner funnel.  
Solution was added to a separatory funnel and the  
lower, aqueous layer was discarded. The upper layer  
was dried over 170.5g of 4Å molecular sieves for 3.5  
25 hr. Solution was filtered by vacuum through a Teflon  
membrane with 1 micron pores set on a glass frit.  
Solution was evaporated on a Buchi rotary evaporator at  
60C. Yield was 35.8g of white solid. Mw was measured  
by GPC as 17,840 AMU with a polydispersity of 7.49.

30

Example 15**Preparation of 20 Mole Percent n-Butylhydridosiloxane**

A 1L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 6000 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 59.9g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL OF ethanol, 25mL of water, and 1000mL Of hexanes were added to the reactor, and stirring was started. 58mL(0.575 mol.) of trichlorosilane and 24mL(0.145 mol.) of n-butyltrichlorosilane (20.2 mol% n-butyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 7.0 RPM. Calculated addition rate was 2.3 mL/min. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171.6g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 38.1g of clear, viscous liquid. Mw was measured by GPC as 16,022 AMU with a polydispersity of 6.45.

30

Example 16

Preparation of 20 Mole Percent  
Cyclohexylhydridosiloxane

A 2L jacketed reactor was fitted with a dry-ice  
5 condenser, a stirrer connected to an Arrow 6000 motor,  
and a glass dip tube. Reactor was connected to a  
recirculating water bath set at 25C. The flask was  
purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown  
across the top of the condenser into an NaOH scrubber.  
10 60.2g of Amberjet 4200(Cl) ion exchange resin catalyst,  
80mL OF ethanol, 25mL of water, and 1000ML of hexanes  
were added to the reactor, and stirring was started.  
59mL(0.585 mol.) of trichlorosilane and 26mL(0.147  
mol.) of cyclohexyltrichlorosilane (20.1 mol%  
15 cyclohexyltrichlorosilane) were combined together in an  
FEP bottle. This mixture of silanes was added to the  
reactor by peristaltic pump through a 1/4" Teflon tube  
at a set rate of 11.0 RPM. Calculated addition rate  
was 2.7 mL/min. After addition was completed, stirring  
20 was continued for 120 min. Solution was filtered by  
vacuum through a Whatman #4 filter in a buchner funnel.  
Solution was added to a separatory funnel and the  
lower, aqueous layer was discarded. The upper layer  
was dried over 172.1g of 4Å molecular sieves for 5 hr.  
25 Solution was filtered by vacuum through a Teflon  
membrane with 1 micron pores set on a glass frit.  
Solution was evaporated on a Buchi rotary evaporator at  
60C. Yield was 42.33g of white solid. Mw was measured  
by GPC as 12,721 AMU with a polydispersity of 7.18.

30

Example 17**Preparation of 20 Mole Percent Phenylhydridosiloxane**

A 1L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 6000 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.2g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL OF ethanol, 25mL of water, and 1000ML of hexanes were added to the reactor, and stirring was started. 58mL(0.575 mol.) of trichlorosilane and 23mL(0.144 mol.) of phenyltrichlorosilane (20 mol% phenyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 7.0 RPM. Calculated addition rate was 2.03 mL/min. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum twice through Whatman #4 filters in buchner funnels. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 171.3g of 4Å molecular sieves overnight. Solution was filtered by vacuum through a Teflon membrane with 20 micron pores set on a glass frit. Solution was then further filtered by vacuum through a Teflon membrane with 5 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 22.2g of white solid. Mw was measured by GPC as 77,827 AMU with a polydispersity of 37.92.

Discussion - Example 3 - Example 17: Dielectric  
Constant Measurements and Cure Temperature Effects

Each of the organohydrogensiloxane resins of  
5 Example 3 through Example 17 were formed into a coating  
solution and spin-coated onto a silicon substrate to a  
nominal thickness of 4000Å. The wafers were cured at  
various temperatures as indicated in Table I below, and  
the dielectric constants for each as-cured polymer film  
10 was measured. The dielectric constants of the cured  
polymer films of the organohydrogensiloxanes of Example  
3 through Example 17, as well as the measured  
dielectric constants for non-organic substituted  
hydrogensiloxane cured films (Controls #1 - #4) is  
15 reported in Table I below. The hydridosiloxane resins  
used in the films reported as Controls #1-#4 were  
prepared in the manner described above.

TABLE I  
Dielectric constant measurements.

Mol % organic substituent used to make resin	Cure Temperature.	Dielectric Constant (at 1 MHz)
Control #1 - No carbon hydridosiloxane	380°C	3.06
20% Methyl (Example 3)	380°C	2.90
20% Methyl (Example 4)	380°C	2.79
Control #2 - No carbon hydridosiloxane	390°C	3.22
4% Methyl (Example 11)	390°C	3.09
8% Methyl (Example 9)	390°C	2.93
12% Methyl (Example 7)	390°C	2.88
16% Methyl (Example 6)	390°C	2.87
20% Methyl (Example 2)	390°C	2.85
Control #3 - No carbon hydridosiloxane	400°C	3.27
20% Methyl (Example 3)	400°C	3.04
20% Ethyl (Example 13)	400°C	2.97
20% Propyl (Example 14)	400°C	2.86
20% n-Butyl (Example 15)	400°C	2.86
20% cyclohexyl (Example 16)	400°C	3.03
20% Phenyl (Example 17)	400°C	2.82
Control #4 - No carbon hydridosiloxane	425°C	3.34
20% Methyl (Example 5)	425°C	3.13

- 5 As can clearly be seen, the dielectric constants in all samples were approximately 3 or lower, and in all cases lower than the non-organic controls. Higher carbon number alkyl moieties and the aryl moiety appear to exhibit lower dielectric constants (i.e., <3). It



is clear to one skilled in the art, in view of Table I, that the higher mole percent carbon-containing substituent polymers have lower dielectric constant values. This is particularly evident in the

5 methylhydridosiloxanes of Example 11, 9, 7, 6, and 2, and in the phenylhydridosiloxane of Example 17.

Table I also clearly shows the effect of cure temperature on the dielectric constant of the as-cured polymer film. Control cells 1, 2, and 3 are carbon-

10 free hydrogensiloxane resins. The reported dielectric constants of the films associated with those Control cells are significantly higher than the dielectric constants of the polymer films formed from the organohydridosiloxanes of Example 3 through Example 17.

15 Moreover, the polymer films of the Control cells exhibit thermal instability and degradation with increasing cure temperature as indicated by the increasing dielectric constants with increasing cure temperature, ranging from 3.06 for Control #1 to 3.34

20 for Control # 4; a difference of 0.28. By comparison, the organohydridosiloxane polymer films of Example 3 through Example 17 remain relatively stable with increasing cure temperature. The higher carbon number substituents seem particularly stable as evidenced by

25 the low dielectric constants associated with Examples 14, 15, and 17.

Examples 18 through Example 20 further describe the synthesis of organohydridosiloxane resins of this invention varying the organic substituent.

30

Example 18**Preparation of 20 Mole Percent t-Butylhydridosiloxane**

A 2L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 6000 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.77g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL OF ethanol, 25mL of water, and 1000ML of hexanes were added to the reactor, and stirring was started. 58mL(0.575 mol.) of trichlorosilane and 27.84g (0.145 mol.) of t-butyltrichlorosilane (20.2 mol% t-butyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 12.3 RPM. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 172.1g of 4Å molecular sieves for 3 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 35.35g of white resin. Mw was measured by GPC as 11,379 AMU with a polydispersity of 4.51.

Example 19**Preparation of 10 Mole Percent Phenylhydridosiloxane**

A 1L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 6000 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 60.3g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL OF ethanol, 25mL of water, and 1000mL Of hexanes were added to the reactor, and stirring was started. 65mL(0.644 mol.) of trichlorosilane and 11.5mL(0.072 mol.) of phenyltrichlorosilane (10 mol% phenyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 10.0 RPM. Calculated addition rate was 2.55 mL/min. After addition was completed, stirring was continued for 20 min. Solution was filtered by vacuum through a Whatman #4 filter in a buchner funnels. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 175.3g of 4Å molecular sieves for 4 hr.. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 30.8g of white solid. Mw was measured by GPC as 16,656 AMU with a polydispersity of 10.23.

30

Example 20**Preparation of 10 Mole Percent t-Butylhydridosiloxane**

A 1L jacketed reactor was fitted with a dry-ice condenser, a stirrer connected to an Arrow 6000 motor, and a glass dip tube. Reactor was connected to a recirculating water bath set at 25C. The flask was purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown across the top of the condenser into an NaOH scrubber. 61g of Amberjet 4200(Cl) ion exchange resin catalyst, 80mL OF ethanol, 25mL of water, and 1000mL Of hexanes were added to the reactor, and stirring was started. 65mL(0.644 mol.) of trichlorosilane and 13.69g (0.071 mol.) of t-butyltrichlorosilane (10 mol% t-butyltrichlorosilane) were combined together in an FEP bottle. This mixture of silanes was added to the reactor by peristaltic pump through a 1/4" Teflon tube at a set rate of 11.0 RPM. After addition was completed, stirring was continued for 120 min. Solution was filtered by vacuum through a Whatman #1 filter in a buchner funnel. Solution was added to a separatory funnel and the lower, aqueous layer was discarded. The upper layer was dried over 173g of 4Å molecular sieves for 4 hr. Solution was filtered by vacuum through a Teflon membrane with 1 micron pores set on a glass frit. Solution was evaporated on a Buchi rotary evaporator at 60C. Yield was 30.75g of white solid. Mw was measured by GPC as 12,112 AMU with a polydispersity of 10.12.

Example 21

Preparation of 20 Mole Percent 3,3,3-  
Trifluoropropylhydridosiloxane

A 1L jacketed reactor was fitted with a dry-ice  
5 condenser, a stirrer connected to an Arrow 6000 motor,  
and a glass dip tube. Reactor was connected to a  
recirculating water bath set at 25C. The flask was  
purged with N<sub>2</sub> and during the reaction N<sub>2</sub> was blown  
across the top of the condenser into an NaOH scrubber.  
10 60.23g of Amberjet 4200(Cl) ion exchange resin  
catalyst, 80mL OF ethanol, 25mL of water, and 1000mL Of  
hexanes were added to the reactor, and stirring was  
started. 58mL(0.575 mol.) of trichlorosilane and  
24mL(0.145 mol.) of 3,3,3-  
15 Trifluoropropyltrichlorosilane (20.1 mol% 3,3,3-  
Trifluoropropyltrichlorosilane) were combined together  
in an FEP bottle. This mixture of silanes was added to  
the reactor by peristaltic pump through a 1/4" Teflon  
tube at a set rate of 7.0 RPM. Calculated addition  
20 rate was 2.05 mL/min. After addition was completed,  
stirring was continued for 120 min. Solution was  
filtered by vacuum twice through Whatman #4 filters in  
buchner funnels. Solution was added to a separatory  
funnel, but no aqueous layer formed. Solution was  
25 dried over 171.64g of 4Å molecular sieves for 4 hr.  
Solution was filtered by vacuum through a Teflon  
membrane with 5 micron pores set on a glass frit.  
Solution was evaporated on a Buchi rotary evaporator at  
60C. Yield was 6.85g of white resin. Mw was measured  
30 by GPC as 27,817 AMU, with a polydispersity of 20.64.

In view of the foregoing, it will be understood  
that the present invention provides a

organohydridosiloxane resin composition having a caged conformation polymer backbone, and therefore essentially no reactive terminal moieties, and up to a 40 mole percent of a carbon-containing substituent. The

5 hydrogen and organic moieties were bonded directly to a silicon atom in the polymer backbone thereby precluding hydrolyzation of the organic moieties, and subsequent chain extension via condensation of the hydroxyl moieties. It is evident that the absence of hydroxyl

10 and alkoxy moieties and the absence of terminal silicon renders the organohydridosiloxanes of this invention very stable in solution, resulting in an extended shelf life. It is also evident that the absence of silanol moieties reduces the dielectric constant of the

15 composition of this invention to a value typically less than three. It is further evident that the presence of organic side groups substantially increases the thermal stability of the composition to a temperature of about 450 °C thereby permitting higher cure temperatures .

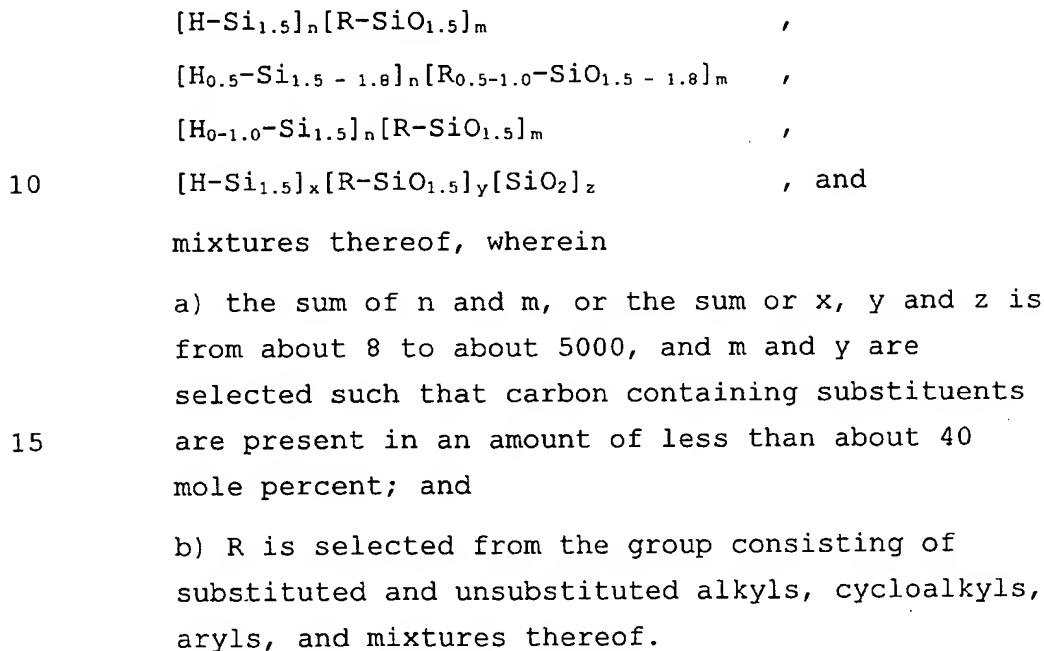
20 The present invention includes a novel process for making the organohydridosiloxane polymer composition of this invention and includes a dual phase solvent system, a non-participating catalyst, and trihalosilane and organo-trihalosilane co-monomers. It is evident

25 that the amount of carbon in the composition is controllable by the relative ratios of the co-monomers. It is also evident that the complete absence of a metal catalyst and the presence of the polar solvent phase renders the product composition of the process

30 extremely pure and free of metal salt, and other ionic contaminants.

WHAT IS CLAIMED IS:

1. A silicon-based polymer, comprising an organohydridosiloxane polymer having a structure  
 5 selected from the group of structures consisting of:



20

2. A silicon-based polymer as in Claim 1 wherein the conformation of said organohydridosiloxane polymer backbone is a cage.
- 25 3. A silicon-based polymer as in Claim 1 wherein said organohydridosiloxane polymer has a molecular weight of between about 400 and about 200,000 atomic mass units (AMU).

4. A silicon-based polymer as in Claim 1 wherein R is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl; cyclohexyl; phenyl; and mixtures thereof.

5. A method for making an organohydridosiloxane, comprising in any operative order:

a) charging a reaction vessel with a dual phase solvent including a non-polar solvent and a polar solvent;

b) adding a monomer solution comprising organotrihalosilanes and hydridotrihalosilanes to the dual phase solvent to provide a reaction mixture;

b) introducing a catalyst to the reaction mixture; and

c) reacting the organotrihalosilanes and hydridotrihalosilanes to form an organohydridosiloxane resin product.

6) A method for making an organohydridosiloxane as in Claim 5 further comprising recovering the organohydridosiloxane resin from the reaction mixture.

7) A method for making an organohydridosiloxane as in Claim 5 wherein said catalyst is selected from a solid phase catalyst and a phase-transfer catalyst solution.

8) A method for making an organohydridosiloxane as in Claim 7 wherein said catalyst is selected from tetrabutylammonium chloride, benzyltrimethylammonium chloride, Amberjet 4200 ion exchange resin, and



Amberlite I-6766 ion exchange resin.

9) A method for making an organohydridosiloxane as in  
Claim 5 wherein said catalyst is Amberjet 4200 ion  
5 exchange resin.

10) A method for making an organohydridosiloxane as in  
Claim 5 wherein said catalyst is tetrabutylammonium  
chloride.

10

11) A method for making an organohydridosiloxane as in  
Claim 5 wherein the hydridotrihalosilane is  
trichlorosilane, and the organo-trihalosilane is  
selected from the group consisting of  
15 methyltrichlorosilane, ethyltrichlorosilane, n-  
butyltrichlorosilane, t-butyltrichlorosilane, n-  
pentyltrichlorosilane, n-hexyltrichlorosilane,  
cyclohexyltrichlorosilane, phenyltrichlorosilane,  
3,3,3-trifluoropropyltrichlorosilane, and mixtures  
20 thereof.

12) A method for making an organohydridosiloxane as in  
Claim 11, wherein said catalyst is Amberjet 4200 ion  
exchange resin.

25

13) A method for making an organohydridosiloxane as in  
Claim 12 wherein said non-polar solvent is selected  
from at least one of pentane, hexane, heptane,  
cyclohexane, benzene, toluene, xylene, and carbon  
30 tetrachloride.

14) A method for making an organohydridosiloxane as in Claim 13 wherein said polar solvent is selected from at least one of water, methanol, ethanol, isopropanol, glycerol, diethyl ether, tetrahydrofuran, and diglyme.

15) A method for making an organohydridosiloxane as in Claim 5 wherein said polar solvent is selected from at least one of water, methanol, ethanol, isopropanol, glycerol, diethyl ether, tetrahydrofuran, and diglyme.

16) A method for making an organohydridosiloxane as in Claim 15 wherein the non-polar solvent is hexane, and the polar solvent is a water and ethanol mixture.

15

17) A method for making an organohydridosiloxane as in Claim 5 wherein the organotrihalosilanes and hydridotrihalosilanes are added to the dual phase solvent in a predetermined ratio for forming an organohydridosiloxane having a predetermined carbon-containing substituent content of between about 0.1 to about 40 mole percent.

18) An organohydridosiloxane composition produced by the process, comprising in any operative order:

a) charging a reaction vessel with a dual phase solvent including a non-polar solvent, and a polar solvent;

b) adding a monomer solution comprising organotrihalosilanes and hydridotrihalosilanes to provide a reaction mixture;

c) introducing a catalyst to the reaction mixture; and

c) reacting the organotrihalosilanes and hydridotrihalosilanes to form an organohydridosiloxane resin product.

5 19) An organohydridosiloxane composition produced by the process of Claim 18 further comprising recovering the organohydridosiloxane from the reaction mixture.

10 20) An organohydridosiloxane composition produced by the process of Claim 18 wherein said catalyst is selected from a solid phase catalyst and a liquid phase-transfer catalyst.

15 21) An organohydridosiloxane composition produced by the process of Claim 20 wherein said catalyst is selected from tetrabutylammonium chloride, Amberjet 4200 ion exchange resin, and Amberlite I-6766 ion exchange resin.

20 22) An organohydridosiloxane composition produced by the process of Claim 21 wherein said catalyst is Amberjet 4200 ion exchange resin.

25 23) An organohydridosiloxane composition produced by the process of Claim 21 wherein said catalyst is tetrabutylammonium chloride.

30 24) An organohydridosiloxane composition produced by the process of Claim 18 wherein the hydridotrihalosilane is trichlorosilane, and the organo-trihalosilane is selected from the group

consisting of methyltrichlorsilane,  
ethyltrichlorosilane, n-butyltrichlorosilane, t-  
butyltrichlorosilane, n-pentyltrichlorosilane, n-  
hexyltrichlorosilane, cyclohexyltrichlorosilane,  
5 phenyltrichlorosilane, and mixtures thereof.

25) An organohydridosiloxane composition produced by  
the process of Claim 24, wherein said catalyst is  
Amberjet 4200 ion exchange resin.

10

26) An organohydridosiloxane composition produced by  
the process of Claim 18 wherein said non-polar solvent  
is selected from at least one of pentane, hexane,  
heptane, cyclohexane, benzene, toluene, xylene, and  
15 carbon tetrachloride.

27) An organohydridosiloxane composition produced by  
the process of Claim 18 wherein said polar solvent is  
selected from at least one of water, methanol, ethanol,  
20 isopropanol, glycerol, diethyl ether, tetrahydrofuran,  
and diglyme.

28) An organohydridosiloxane composition produced by  
the process of Claim 21 wherein said polar solvent is  
25 selected from at least one of water, methanol, ethanol,  
isopropanol, glycerol, diethyl ether, tetrahydrofuran,  
and diglyme.

29) An organohydridosiloxane composition produced by  
30 the process of Claim 28 wherein said non-polar solvent  
is selected from at least one of pentane, hexane,  
heptane, cyclohexane, benzene, toluene, xylene, and

carbon tetrachloride.

30) An organohydridosiloxane composition produced by the process of Claim 29 wherein the polar solvent is hexane, and the non-polar solvent is a water and ethanol mixture.

31) An organohydridosiloxane composition produced by the process of Claim 18 wherein the organotrihalosilanes and hydridotrihalosilanes are added to the dual phase solvent in a predetermined ratio for forming an organohydridosiloxane having a predetermined carbon-containing substituent content of between about 0.1 to about 40 mole percent.

15

32) A silicon-based polymer, comprising an organohydridosiloxane polymer having the structure:



wherein

- 20 a) the sum of n and m is from about 8 to about 5000, and m is selected such that carbon containing substituents are present in an amount of less than about 40 mole percent; and
- 25 b) R is selected from the group consisting of substituted and unsubstituted alkyls, cycloalkyls, aryls, and mixtures thereof.

33) A silicon-based polymer as in Claim 32 wherein R is methyl.

30

34) A silicon-based polymer as in Claim 33 wherein the

mole percent of methyl-containing substituent is  
between about 15 mole percent to about 25 mole percent.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 98/06490

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08G77/12 C08G77/04

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 106 604 A (AGASKAR PRADYOT) 21 April 1992 see claims 1-5 see column 2, line 25 - line 57 ---	1-6, 18, 32
X	EP 0 419 076 A (DOW CORNING) 27 March 1991 see claim 1 see page 2, line 49 - page 3, line 4 see page 5, line 2 - line 26 ---	1-4, 32
A	EP 0 516 144 A (DOW CORNING TORAY SILICONE) 2 December 1992 see claims 1, 2 see page 2, line 11 see page 4, line 20 - line 41 --- -/--	1-6, 32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
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Date of the actual completion of the international search

24 June 1998

Date of mailing of the international search report

02/07/1998

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# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 98/06490

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 599 209 A (DOW CORNING TORAY SILICONE) 1 June 1994 see claims 1-10 ---	1
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